

THERMOELECTRIC PROPERTIES OF SELENIDES SPINELS

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ABSTRACT

Many compounds with the spinel structure type have been analyzed for their thermoelectric properties. Published data was used to augment experimental results presented here to select promising thermoelectric spinels. Compounds studied here include $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$ and CuIr_2Se_4 . Many exhibit low lattice thermal conductivity of about 20 mW/cmK, independent of temperature. Two series of compounds were selected for further study: $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and $\text{Zn}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ and preliminary results are given.

INTRODUCTION

The growth of commercial applications of thermoelectric devices depends primarily on increasing the figure of merit, ZT , for thermoelectric materials. The figure of merit is defined as $ZT = \alpha^2 \sigma T / \lambda$, where α is the Seebeck coefficient, σ the electrical conductivity, λ the thermal conductivity, and T is the absolute temperature. Materials with a large $\alpha^2 \sigma$ value, or power factor, are usually heavily doped semiconductors, such as Bi_2Te_3 . The thermal conductivity of semiconductors is usually dominated by phonon or lattice thermal conductivity. Thus, one method for finding new, advanced thermoelectric materials is to search for semiconductors with low lattice thermal conductivity.

In this paper we evaluate compounds based on the Spinel structure with general composition $\text{A}_1\text{B}_2\text{X}_4$ where A and B are transition metals and X is a chalcogen, primarily Se. Previous work on such compounds [1] have shown that a range of metals and insulators exist with this structure type.

The structure of Spinel (Figure 1) consists of cubic close packed chalcogen atoms with metal B atoms in half the octahedral holes and metal A atoms in 1/8 of the tetrahedral holes. There can be significant mixing of the different metal atoms on the two metal sites. As suggested by Spitzer [2] the relatively high coordination number of the B atoms in this structure may favor low lattice thermal conductivity. The large cubic unit cells (about 10\AA) full of vacant octahedral holes should reduce the lattice thermal conductivity by increasing the scattering of phonons. The

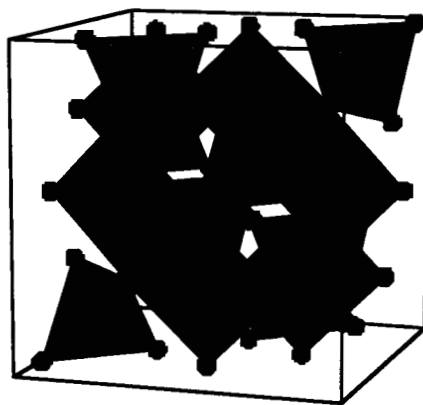


Figure 1. Illustration of the Spinel unit cell (e.g. ZnCr_2Se_4) showing Se atoms as spheres Cr atoms (not shown) at the center of the shaded octahedra and Zn atoms (not shown) at the center of the shaded tetrahedra. The cubic unit cell is indicated.

spinel semiconductors have been made by doping with about one percent of a +1 or +3 element on the A⁺² site, such as with CdCr₂Se₄ [6, 7] or HgCr₂Se₄ [8] where a RT power factor of about 1 $\mu\text{W}/\text{cmK}^2$ was found [9]. CuCr₂Se₄ like its S counterpart is metallic and can be used not only to dope but also alloy with the insulating chromium spinels such as Cd_xCu_{1-x}Cr₂Se₄[10] (maximum RT power factor 10⁻⁴ $\mu\text{W}/\text{cmK}^2$) and Ga_xCu_{1-x}Cr₂Se₄[11]. Such solid solutions are often not completely miscible, forming two spinel phases with different crystallographic cells [12, 13] particularly when the two types of A ions differ in size.

Table 1. Room Temperature thermoelectric properties of S or Se spinel compounds reported in the literature [1, 5, 14, 15]. I indicates insulating.

| Composition | ρ_{300} m Ωcm | Seebeck $\mu\text{V}/\text{K}$ | $\Delta E_{\text{optical}}$ eV | $\Delta E_{\text{resistivity}}$ eV | Mobility cm^2/Vs |
|--|-------------------------------------|-----------------------------------|-----------------------------------|---------------------------------------|-------------------------------------|
| FeCr ₂ S ₄ | I | - | | 0.02 - 0.2 | 0.3 |
| CoCr ₂ S ₄ | I | - | | 0.01 - 0.3 | 0.2 |
| MnCr ₂ S ₄ | I | - | | 0.1 - 0.3 | |
| ZnCr ₂ S ₄ | I | - | | 0.6 | |
| CdCr ₂ S ₄ | I | - | 1.6 | 0.2-0.6 | |
| HgCr ₂ S ₄ | I | - | 1.4 | 0.4 - 2 | |
| Ni _{0.5} Co _{0.5} Cr ₂ S ₄ | 200 | 60 | | 0 - 0.12 | 1 |
| CuCr ₂ S ₄ | 0.9 | 16 | | 0.03 | |
| CuV ₂ S ₄ | 0.6 | 5 | | | |
| CuTi ₂ S ₄ | 0.4 | -12 | | | |
| CuCo ₂ S ₄ | 0.4 | 13 | | | |
| NiCo ₂ S ₄ | 0.8 | -18 | | | |
| CoNi ₂ S ₄ | 0.4 | -2 | | | |
| Co ₃ S ₄ | 0.3 | 5 | | | |
| ZnCr ₂ Se ₄ | I | - | 1.3 | 0.3 | 5 |
| CdCr ₂ Se ₄ | I | - | 1.3 | 0.2 - 0.6 | 50 |
| HgCr ₂ Se ₄ | I | - | 0.84 | 0.4 - 2 | 30 |
| CuCr ₂ Se ₄ | 0.1 | 16 | | | <10 |
| CuIr ₂ Se ₄ | 5 | | | | |

Using these previous results, we prepared compositions that looked promising for thermoelectric applications and/or where thermoelectric data was missing.

Polycrystalline samples were prepared by mixing and reacting elemental powders in evacuated silica ampoules for several days at 700° - 800° C. The samples were analyzed by x-ray diffractometry to confirm the crystalline structure. The powders were then hot-pressed in graphite dies into dense samples, 3 mm long and 12 mm in diameter. The hot-pressing was conducted at a pressure of 1400 kg/cm² and 700° - 800° C for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be greater than 90% of the theoretical density for all samples.

The samples were also characterized by microprobe analysis which was performed using a JEOL JXA-733 electron superprobe. The Al and In concentration in the samples of Cu_{0.5}In_{0.5}Cr₂Se₄ and Cu_{0.5}Al_{0.5}Cr₂Se₄ were not uniform. The CuIr₂Se₄ contained some (~10%)

IrSe₂ secondary phase. The elemental concentrations determined from microprobe analysis for Ga_xCu_{1-x}Cr₂Se₄ were within a few atomic percent of the expected values.

Table 2. Room temperature thermoelectric properties from this study. I indicates insulating. FM indicates Ferromagnetic.

| Composition | ρ_{300} m Ω cm | Seebeck μ V/K | Th. con mW/cmK | Mobility cm ² /Vs |
|---|-------------------------------|----------------------|-------------------|---------------------------------|
| FeCr ₂ Se ₄ | 2×10^4 | 400 | 28 | 0.1 |
| ZnCr ₂ Se ₄ | I | - | 31 | 2 |
| CdCr ₂ Se ₄ | I | - | 30 | <5 |
| Cu _{0.5} Al _{0.5} Cr ₂ Se ₄ | 30 | 100 | 16 | 6 |
| Cu _{0.5} In _{0.5} Cr ₂ Se ₄ | 30 | 300 | 20 | 16 |
| Cu _{0.5} Co _{0.5} Cr ₂ Se ₄ | 0.6 | 30 | 25 | 10 |
| CuSnCrSe ₄ | 10 | 100 | 20 | 5 |
| CuCr ₂ Se ₄ | 0.28 | 25 | 37 | FM |
| CuIr ₂ Se ₄ | 0.3 | 3 | | -2 |

Samples in the form of disks (typically a 1.0 mm thick, 12 mm diameter slice) were cut from the cylinders using a diamond saw for electrical and thermal transport property measurements. Temperature dependence of electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity and heat capacity measurements were conducted on selected samples between 80 and 800K. The resistivity and Hall effect were measured using the method of Van der Pauw [16]. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by $n = 1/R_H e$, where n is the density of holes or electrons, and e is the electron charge. The Hall mobility (μ_H) was calculated from the Hall coefficient and the resistivity values by $\mu_H = R_H/\rho$. The Hall effect, however, is often compounded by the anomalous Hall effect because of ferromagnetism in many of the compounds. Therefore it is often difficult to estimate the Hall mobility or carrier concentration. The Seebeck coefficient (α) was measured with a high temperature light pulse technique [17]. Room temperature thermal conductivity was measured using the comparison method [18]. High temperature heat capacity and thermal diffusivity were measured using a flash diffusivity technique [19]. The thermal conductivity (λ) was calculated from the experimental density, heat capacity, and thermal diffusivity values.

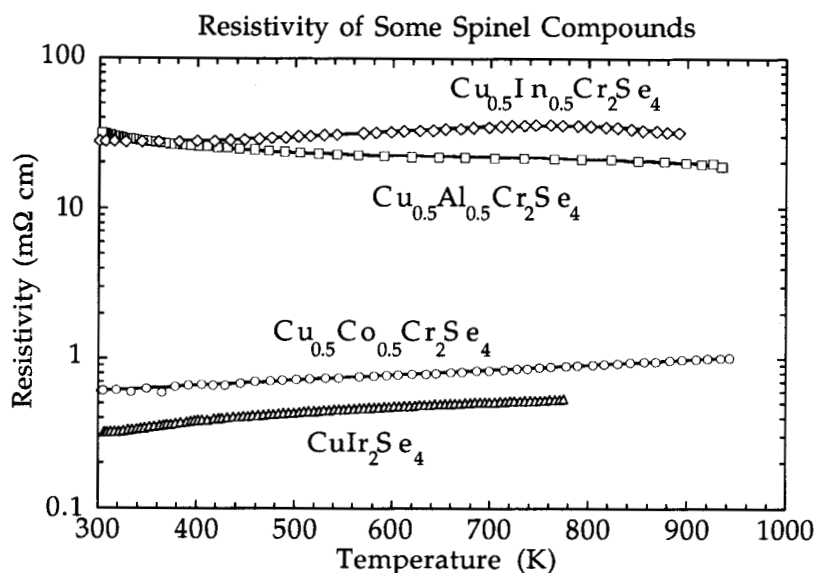


Figure 3. Electrical Resistivity of some Spinel compounds.

Results and Discussion

The Spinel selenides and sulfides exhibit a wide variety of electronic properties (Tables 1 and 2). Some, CuIr_2Se_4 and $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{Se}_4$ for example, are metals (resistivity increases with temperature) having room temperature resistivity (ρ) from about 10^{-4} to $10^{-3} \Omega\text{cm}$. Others, such as the alloys $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$ and $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$, are semimetals or very low band gap semiconductors with high carrier concentrations. Spinel having a stable +2 A atom, are usually insulators or high band gap (~ 1 eV optical gap) semiconductors. These semiconductors can then be doped n or p-type. Measurements in the resistivity and thermopower as a function of temperature frequently contain discontinuities and hysteresis (hysteretic samples not shown), which may be due to magnetic or structural changes, or even loss of S or Se at high temperatures.

Exchange split Cr^{+3} in octahedral coordination will have 3 electrons to completely fill the majority spin T_{2g} orbital (or subsequent band); thus Cr^{+3} may not provide metallic carriers. This is certainly the case for the insulating chromium spinels in Tables 1 and 2. The doping or alloying on the A site should produce doped semiconductors or metals. However, significant alloying on the A site may result in a polaron semiconductor instead of a metal due to the localization effects of the distant dopant atoms. Such behavior is more clearly demonstrated in the related defect NiAs-type ACr_2Se_4 chromium selenides [3, 20].

The resistivity due to small polaron hopping conduction has only a slightly different temperature dependence ($T \exp(E_a/kT)$) than that expected of a semiconductor ($\mu^{-1} \exp(E_a/kT)$ where the mobility μ is proportional to $T^{-3/2}$ for many semiconductors). Both forms are dominated by an exponential with characteristic energy E_a . For the materials described here the resistivity data is not sufficiently well described by either of the exact forms to determine the transport mechanism. Nevertheless, band semiconductor transport characteristically has carriers with high mobility and low concentration while small polarons have high concentration and low mobility. Thus, the data suggests that these materials have polaron conductivity.

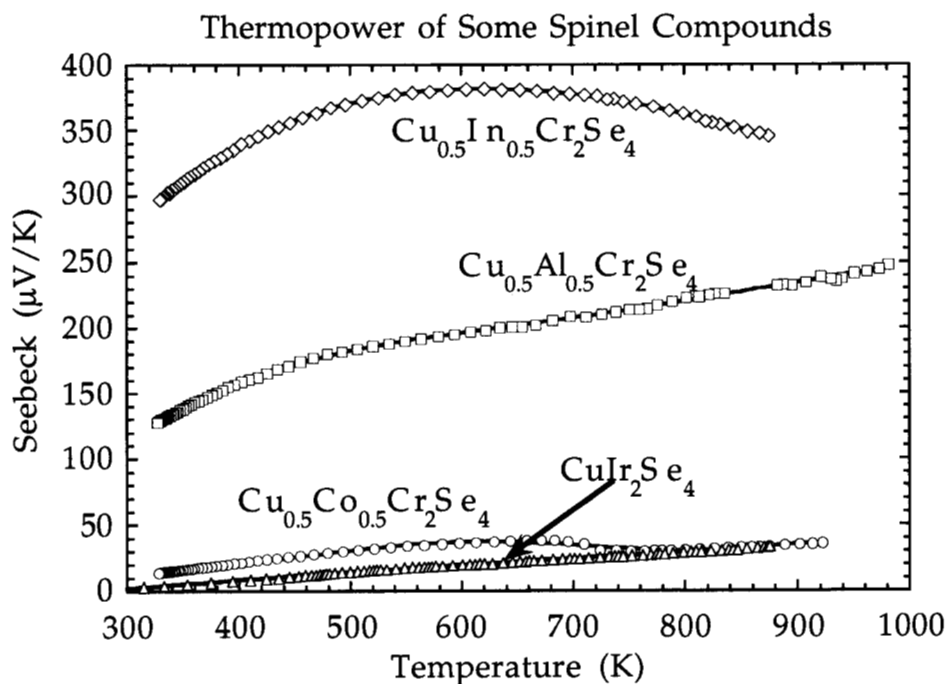


Figure 4. Thermopower of some Spinel compounds.

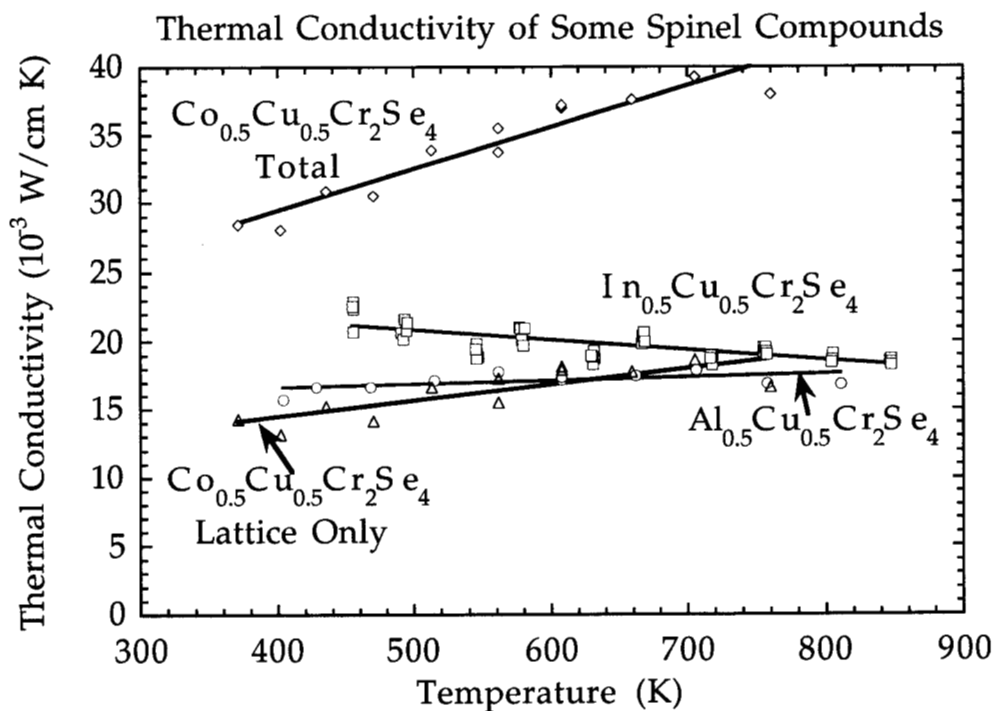


Figure 5. Thermal Conductivity of some Spinel compounds.

The thermopower of some of the spinel compounds studied is shown in Figure 4. The low resistivity samples have metallic like that are low and linear. The higher resistivity samples can have large thermopowers like conventional semiconductors, even though transport is probably by small polarons.

The thermal conductivity λ is given by the sum of the electronic λ_E and lattice contributions λ_L . λ_E is directly related to the electronic conductivity: $\lambda_E = L\sigma T$, where L is the Lorenz factor. The Lorenz factor used is that typical for metals ($2.4 \times 10^{-8} \text{ J}^2/\text{K}^2\text{C}^2$). The measured thermal conductivity of some spinel compounds is shown in Figure 5. The electronic contribution of the high resistivity samples ($\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$ and $\text{Cu}_{0.5}\text{Al}_{0.5}\text{Cr}_2\text{Se}_4$) is not significant ($< 1 \text{ mW/cm K}$) so the measured values are due to the lattice contribution.

The lattice thermal conductivity is relatively independent of temperature (Figure 7) indicating multiple scattering processes. Low, temperature independent thermal conductivity is found in complex structures such as glasses. Common crystalline materials have large lattice thermal conductivity that is proportional to $1/T$. The quaternary spinel compounds should have lower lattice thermal conductivity because of additional alloy scattering.

The power factor and therefore figure of merit is relatively low for most of these compounds. These materials should have carriers with high effective masses, that improve the thermoelectric properties, but the very low Hall mobilities of these carriers cancels any improvement. Typical thermoelectric materials have Hall mobilities greater than $10 \text{ cm}^2/\text{Vs}$, whereas the materials in Table 2 have mobilities at least 10 times less. This may be due to the hopping method of transport, the increased electron scattering from the transition metal magnetic moments (magnon scattering) or due to the lower covalency of these materials as compared to conventional thermoelectric semiconductors.

The spinels with the most promising thermoelectric properties are derivatives of CuCr_2Se_4 . Our next task is to select a representative series of compounds to study that we think may give good thermoelectric properties with optimal doping or alloying. The series of compounds $\text{Fe}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ [4] and $\text{Cd}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ [10] have been studied in the composition ranges appropriate for thermoelectric materials with some promising results. The compounds $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ [11] should be semiconducting at $x = 1/2$ assuming Ga is +3 and Cu is +1. The alloys should produce both p- and n-type compositions, depending on whether $x < 1/2$ or $x > 1/2$ respectively. We found that the related series $\text{In}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ makes two phase samples with the major phase being $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{Se}_4$. A previous study of $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ [11] did not investigate bulk samples in the composition range useful for thermoelectrics. Thus we chose to examine the series $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$.

The other series of samples being studied is $\text{Zn}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$. The parent compound ZnCr_2Se_4 undergoes magnetic ordering at low temperature. From band structure calculations [21] it was suggested that in the ordered state the magnon scattering will no longer hinder the mobility, but will still have the high effective mass carriers with large thermopower.

$\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ Electrical Resistivity

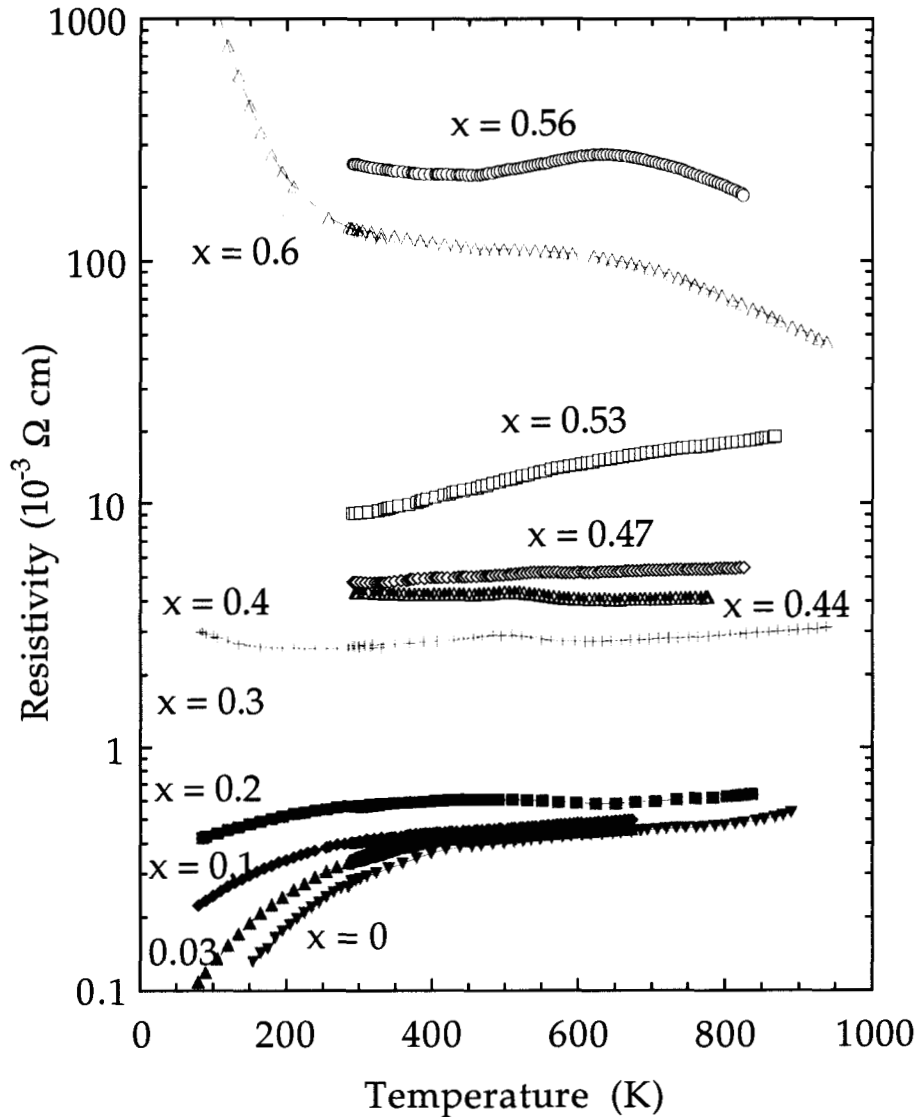


Figure 6. Electrical resistivity of $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ for various x .

The resistivity of $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ for various x is shown in Figure 6. There is a change in slope at the ferromagnetic curie temperature in samples with small x . This transition temperature decreases from 435K for $x = 0$ to about 375K for $x = 0.1$. There is another transition observable in the resistivity between 475K and 525K for $0.2 < x < 0.5$. This other transition appears to broaden and move to even higher temperature for $x > 0.5$.

The thermopower of $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ for various x is shown in Figure 7. As expected, the p-type range extends up to approximately $x < 0.5$, gradually changing from a p-type metal with linear seebeck coefficient to a p-type semiconductor with a peaked seebeck coefficient. The n-type region, however, is small because the spinel structure is not stable for x above about 0.6. The room temperature thermoelectric properties are shown in Figure 8, highlighting the metal-insulator transition and p-type to n-type transition at around $x = 0.55$.

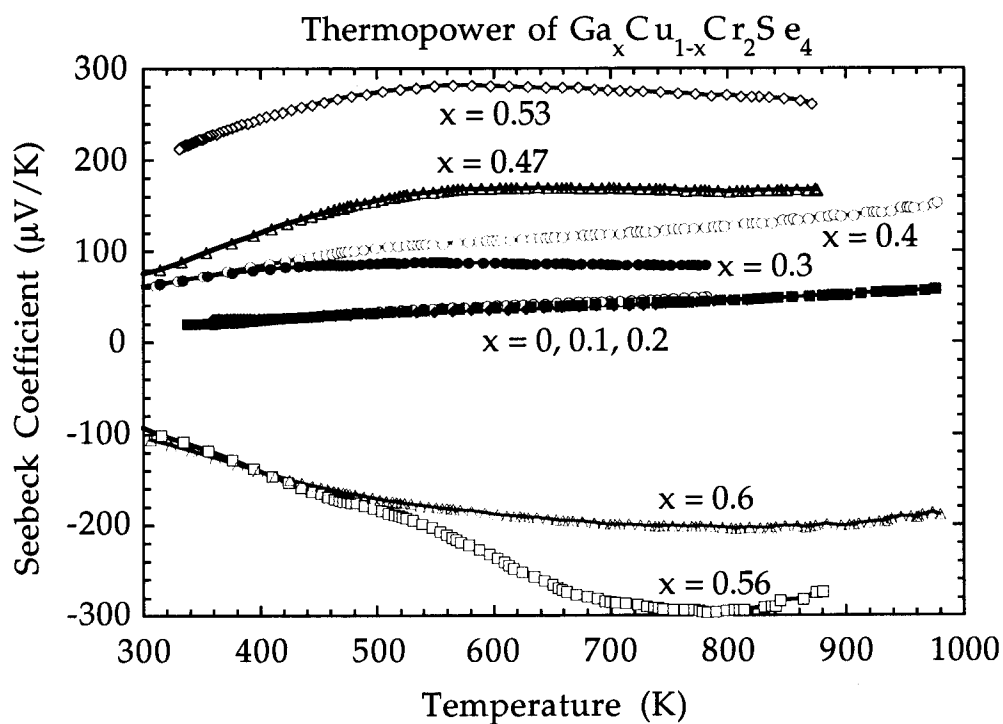


Figure 7. Thermopower of $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ for various x .

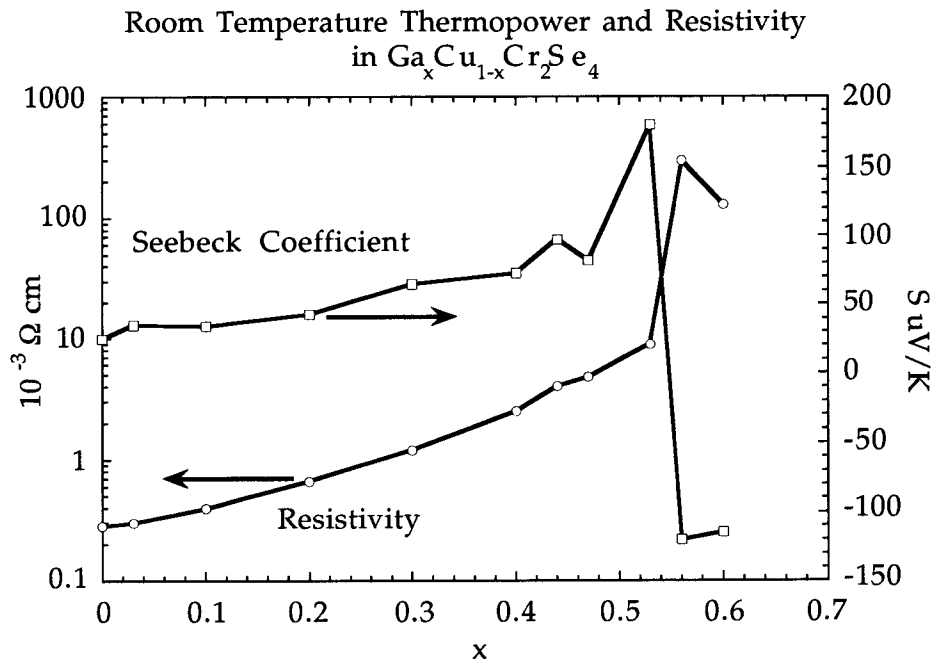


Figure 8. Room temperature values of electrical resistivity and thermopower for $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$.

The room temperature values are also plotted in Figure 9 along with other $A_xCu_{1-x}Cr_2Se_4$ compounds for comparison. The room temperature values for p-type $Ga_xCu_{1-x}Cr_2Se_4$ fall near the line of constant $3 \mu W/K^2$ power factor, indicating that these compounds have about the same thermoelectric figure of merit at this temperature. This power factor is significantly higher than that previously reported for $Ga_xCu_{1-x}Cr_2Se_4$ [11] on single crystals and $Cd_xCu_{1-x}Cr_2Se_4$ [13], but comparable to our preliminary results on $Zn_xCu_{1-x}Cr_2Se_4$. The maximum figure of merit, shown in Figure 10, is about 0.1 for the p-type compounds, which is comparable to that found in the defect NiAs - type series of compounds $Fe_xCr_{3-x}Se_4$ [20].

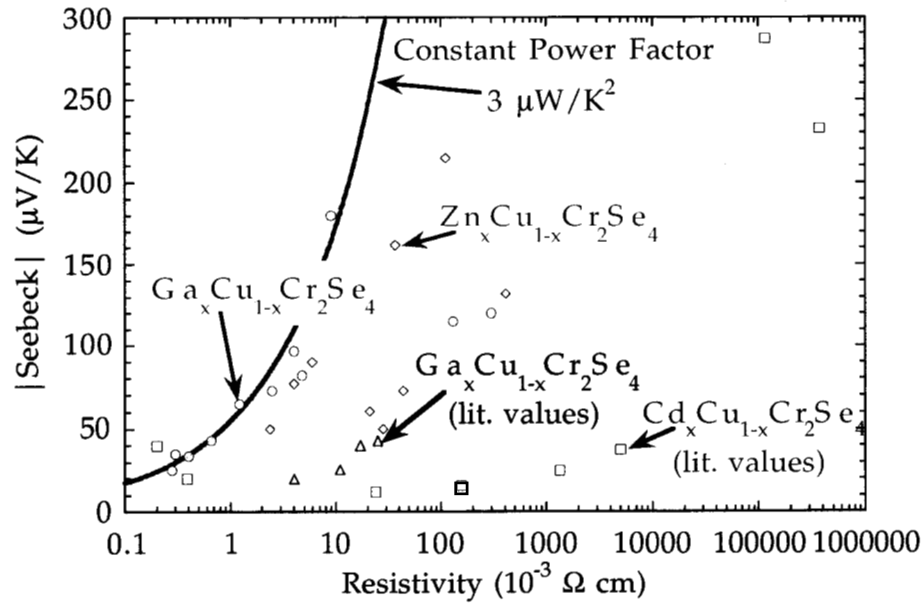


Figure 9. Room temperature values of electrical resistivity and thermopower for various $A_xCu_{1-x}Cr_2Se_4$. Samples with a high power factor ($\alpha^2\sigma$) are to the upper left, those with a low power factor to the lower right. A iso-line of constant power factor is shown. The literature values are obtained from [11, 13].

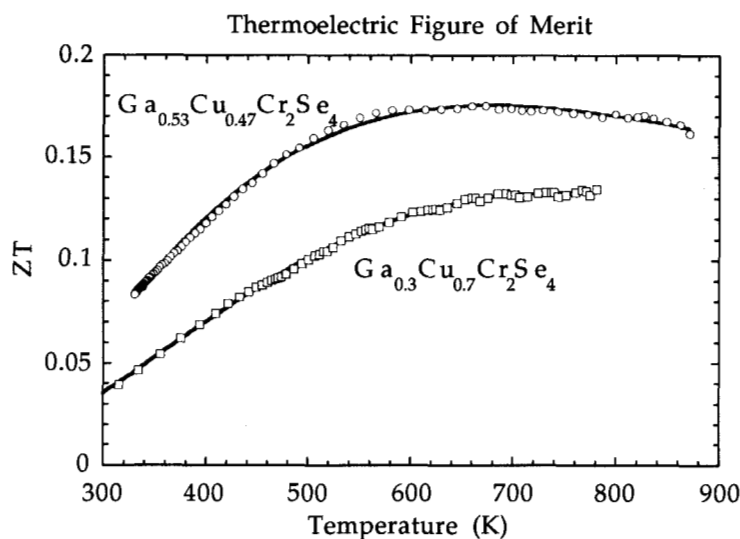


Figure 10. Thermoelectric figure of merit, ZT , for $x = 0.3, 0.53$ in $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$.

Summary

A variety of spinel sulfides and selenides were examined for high thermoelectric figure of merit. Reported thermoelectric properties and the existence of known compounds helped guide the selection of materials to reexamine. Many showed low, glass-like thermal conductivities. Most compounds not containing chromium were eliminated due to their strongly ionic character (sulfides and rare earth selenides). Others show a variety of electronic properties from metals to small polaron semiconductors, with low carrier mobilities. A representative series of compounds $\text{Ga}_x\text{Cu}_{1-x}\text{Cr}_2\text{Se}_4$ has been studied to examine the doping region of interest for thermoelectric applications. Both p- and n-type compounds have been found; the maximum figure of merit ZT is of order 0.1.

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REFERENCES

- [1] *Landolt-Börnstein* Springer-Verlag, Berlin, Vol. NS III/17h; NS III/12b; NS III/4b.
- [2] D. P. Spitzer, *J. Phys. Chem. Solids* **31**, 19 (1970).
- [3] G. J. Snyder, T. Caillat, and J.-P. Fleurial, *MRS Proceedings* **545**, Z9.4 (1999).
- [4] F. K. Lotgering, R. P. vanStapele, G. H. A. M. vanderSteen, *et al.*, *J. Phys. Chem. Solids* **30**, 799 (1969).
- [5] T. Furubayashi, T. Kosaka, J. Tang, *et al.*, *J. Phys. Soc. Jpn.* **66**, 1563 (1997).
- [6] H. W. Lehmann, *Phys. Rev.* **163**, 488 (1967).
- [7] A. Amith and G. L. Gunsalus, *J. Appl. Phys.* **40**, 1020 (1969).
- [8] M. R. Chaves, J. L. Ribeiro, A. Selmi, *et al.*, *Phys. Stat. Sol.* **92**, 263 (1985).

- [9]K. Minematsu, K. Miyatani, and T. Takahashi, J. Phys. Soc. Jpn. **31**, 123 (1971).
- [10]H. Duda, T. Gron, and J. Warczewski, J. Magn. Magn. Mater. **88**, 55 (1990).
- [11]T. Gron, K. Baerner, C. Kleeberg, *et al.*, Physica B **225**, 191 (1996).
- [12]H. D. Lutz, U. Koch, and I. Okonska-Kozłowska, J. Solid State Chem. **51**, 69 (1984).
- [13]J. Krok-Kowalski, H. Rej, T. Gron, *et al.*, J. Magn. Magn. Mater. **137**, 329 (1994).
- [14]R. J. Bouchard, P. A. Russo, and A. Wold, Inorg. Chem. **4**, 685 (1965).
- [15]A. A. Abdurragimov, Z. M. Namazov, L. M. Valiev, *et al.*, Inorg. Mater. **17**, 1113 (1981).
- [16]L. J. van der Pauw, Philips Res. Repts. **13**, 1 (1958).
- [17]C. Wood, L. D. Zoltan, and G. Stapfer, Rev. Sci Instrum. **56**, 719 (1985).
- [18]D. M. Rowe, *Thermoelectric Handbook* (CRC, Boca Raton, 1995).
- [19]J. W. Vandersande, C. Wood, A. Zoltan, *et al.*, in *Thermal Conductivity* (Plenum, New York, 1988), p. 445.
- [20]G. J. Snyder, Submitted.
- [21]D. Singh, Private Communication.